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WOOD NAVAL STORES - AN INDUSTRIAL WASTE GUIDE TO THE WOOD NAVAL STORES INDUSTRY

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

May 1952

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FEDERAL SECURITY AGENCY
Public Health Service
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Wood Naval Stores Industry

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INDUSTRIAL WASTE GUIDE

WOOD NAVAL STORES

Introduction

Naval stores are produced by the refining of oleoresinous materials from pine wood and may be divided into two broad classes: (1) gum naval stores, obtained by simple steam distillation of the exudate from living pine trees, and (2) wood naval stores, obtained from dead pine wood and stumps. Wood naval stores are further divided into three categories: (a) destructively distilled wood naval stores, (b) sulfate wood naval stores, and (c) steam-distilled wood naval stores.

The basic products of the gum branch are gum spirits of turpentine and gum rosin. Destructive distillation of pine wood yields turpentine, pine oil, pine tar, and a charcoal residue. The refining of the volatile oils recovered from the digestion of pine wood by the sulfate paper manufacturing process results in sulfate wood turpentine. This process produces no rosin, but acidification of the digestion liquors yields a liquid rosin, known as tall oil, which is a mixture of resin acids and fatty acids. Steam-distilled wood naval stores are produced by steam-and-solvent extraction of shredded pine stumps. The resulting products are steam-distilled wood turpentine, pine oil, dipentene and rosin. Further refining of the basic products obtained by all four methods will yield additional, more valuable commodities.

The volume and pollutional characteristics of the liquid wastes associated with the naval stores industry vary with the method of production. By far the most voluminous and variable are those resulting

from the steam and solvent extraction process. This guide is primarily concerned with the wastes resulting from this phase of the wood naval stores branch.

In 1951 a total of 2,500,000 tons of pine stumps were processed, which resulted in a reported production of:

1,399,410 drums[1] of steam-distilled wood rosin,
237,080 barrels[2] of steam-distilled wood turpentine,
8,659,000 gallons of pine oil,
2,232,000 gallons of dipentene, and
2,527,000 gallons of other monocyclic hydrocarbons

[1] 520 pounds net weight each
[2] 50 gallons each

Steam-distilled wood naval stores are manufactured at fourteen plants in five Gulf Coast states. Mississippi has six operating plants and Louisiana four. Production from these two states, however, is nearly equal. Two plants are located in Alabama and one each in Florida and Georgia. Construction of another plant in Alabama and one or more in the Pacific Northwest is planned for the near future.

Liquid wastes from the existing fourteen wood naval stores plants are estimated to have a population equivalent of 800,000 based on 5-day B.O.D.

Manufacturing Processes

The primary process for extracting and refining pine products from pine stumps is basically the same in all plants. In contrast with the gum branch of the industry, the wood plants operate continuously, 24 hours per day, rather than seasonally. The capacities of the wood plants range from 200 to 1,000 tons of stumps processed per day.

The principal raw materials are the stumps and deadwood of two species of southern pine - longleaf yellow (Pinus palustris Miller) and slash (Pinus caribaea Morelet) - which were left in the ground from prior lumbering operations. The wood structure is largely heartwood with comparatively thin sapwood. The heartwood is saturated with terpenes and resins that make it almost impervious to attack by insects, fungi or rot. Stumps that have been in or on the ground ten to fifteen years or more are preferred, as they are easier to reduce to proper size for extraction. The average composition of seasoned pine stumps includes 22 per cent moisture, 5 per cent volatile oils, 22 per cent rosin, and 51 per cent ligneous and cellulose materials.

Pine stumps are dislodged from the ground by pushdozers or dynamite and delivered to the plant by truck or rail. A sufficient supply of stumps to last six months to one year is stockpiled for use when field activities are halted due to unfavorable weather.

Chain conveyors move the stumps to a washer where dirt, sand and loose or rotted wood are removed. The volume of wash water used and the efficacy of washing differ with the plants. This procedure varies from a mild water spray to violent agitation and spray in a tumbler barrel. Washer waste water is passed through coarse screens for recovery of large wood fibers before being discharged. A few plants recycle this water after screening and settling. Stump washing activities are normally confined to 16 hours out of 24.

The clean stumps are fed directly to grinding equipment consisting of hogs and shredders which deliver wood chips 1/2 to 1-1/2

inches in length and 1/8 to 1/4 inch diameter. This size is considered optimum, allowing the maximum rate of extraction with a minimum difficulty in handling. The chips are conveyed to fresh chip storage to await processing.

Fresh chips from storage are moved by belt conveyors to the extractors which are large pressure vessels holding from 5 to 15 tons of chips. All plants are equipped with from 10 to 20 of these extractors, although at any one time only 7 to 10 are in the extraction phase. Different extraction solvents can be used. Twelve of the fourteen plants use a narrow range petroleum fraction (200-240°F naphtha) and two use coal tar hydrocarbons - largely benzene.

At a temperature ranging between 260 and 300°F, the solvent is pumped into the bottom of the first extractor, from the top of this to the bottom of the second, proceeding thus through the cycle. Extractor pressures range from 65 to 100 psi gage. Solvent is pumped through the cycle until 10,000 to 20,000 gallons have passed through the last extractor. At this time the first extractor is cut out of the cycle and a fresh one added. The spent extractor is steamed for the recovery of solvent and oils. In this system the fresh solvent is introduced into the extractor containing the most exhausted chips and the loaded solvent is passed through the freshest chips. The spent chips are removed manually and pass to spent chip storage until needed for fuel to produce steam for process use and electric power generation.

The crude solution of rosin, solvent, and terpene oils, known

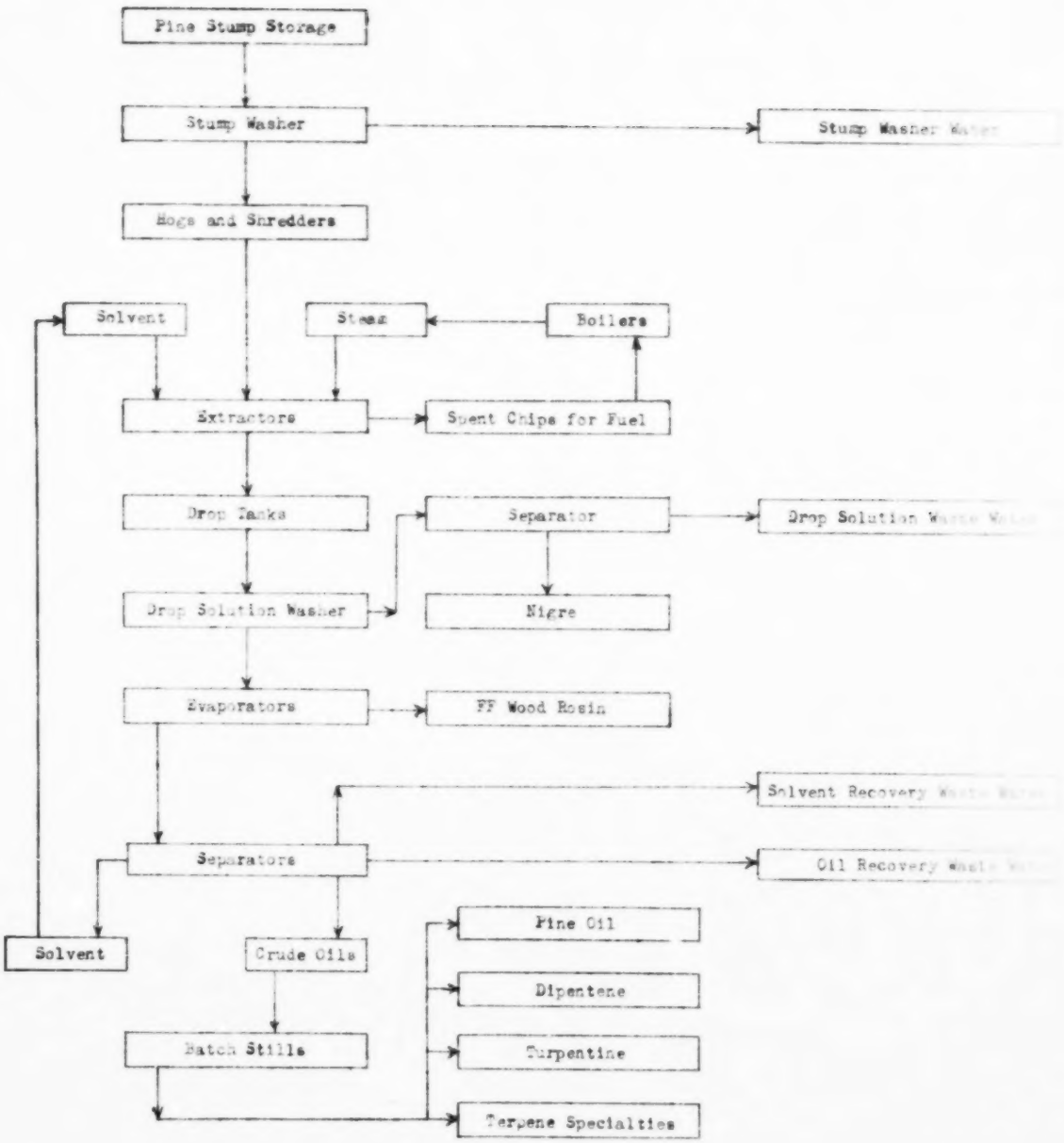
as "drop solution," is pumped to storage tanks to await refining. A small amount of water separates from the oils in these tanks and is wasted.

The drop solution can be processed by various methods, all resulting in the same end-products. In the arrangement used most often, the crude solution is pumped to wash tanks where water sprays directed into the solution from the top of the tanks wash out color bodies. From the base of the wash tanks a heavy, dark resin, known as "nigre," is periodically drawn off. The water used in washing the crude solution is released continuously from the base of the tanks. The remaining solution is passed to evaporators where the solvent is removed and returned to storage tanks for re-use. A system of successive equilibrium distillations removes the terpene oils, leaving a marketable residue known as FF wood rosin. The terpene oils are charged to batch stills where the oils are fractionated into turpentine, pine oil, dipentene and other terpene specialties. Figure 1 is presented as a simplified flow diagram showing the primary operations and liquid wastes of a wood naval stores plant.

An alternate procedure, used at some plants, is to separate the oils from the drop solution before removing the nigre from the rosin.

When benzene is used as the extraction solvent, the crude solution yield is greater, at a sacrifice in color, and is subsequently refined in a different manner than that already described. From the drop tanks, the crude solution is pumped to a still house to be separated in fractionating columns into three fractions: recovered

Figure 1
Flow Diagram
Wood Naval Stores Plant
Naphtha Solvent Extraction
Primary Process



solvent, crude oils, and crude rosin. The solvent is returned to the system and the crude oils are refined by fractional distillation into the desired cuts.

The crude rosin, free from oils, is further treated, while hot, with gasoline and furfuraldehyde to remove the color bodies. The rosin is recovered from solution by suitable evaporators. This method results in a pale-grade rosin, which is more valuable than FF wood rosin, and a dark residue comparable to the nigre from the naphtha extraction system.

Secondary rosin refining units to produce more valuable resins are in operation at a few of the plants. These processes include pale-grade rosin refining, polymerization, disproportionation, hydrogenation, isomerization, synthesization, and manufacture of metallic resinates. Secondary refining is conducted at a majority of the plants but in most cases on a limited scale.

In pale-grade rosin refining, FF wood rosin in naphtha solution is pumped to adsorption towers where color reduction is accomplished by adsorption in magnesium trisilicate. The volume moved through the towers depends on the color grade of the rosin desired.

The pale rosin solution is passed to evaporators where the naphtha is recovered. The rosin, containing small quantities of terpene oils, moves to a fractionator where the oils are recovered.

As a by-product of pale rosin refining, a rosin containing the color bodies is removed from the magnesium tricilicate by washing with alcohol. The alcohol-rosin solution is passed to evaporators where the alcohol is recovered. The dark rosin is fractionated for recovery of oils and the resulting residue is marketed as B wood rosin.

Polymerized rosin is produced by treating refined rosin with sulfuric acid, in benzene solution, under controlled conditions of temperature, concentration, and contact. Under these conditions, about one-third of the rosin acids present unite to form polymers. The resulting resin is superior to the rosin from which it was made.

Disproportionated (dehydrogenated) rosin is the resulting product from the heating of refined rosin in the presence of a catalyst. This reaction changes abietic acid to the dihydroabietic, tetrahydroabietic and dehydroabietic forms, and is generally referred to as dehydrogenation. This rosin is normally made into soap or paper size by mixing with an alkali in batch kettles.

Hydrogenated rosin is produced by treating refined rosin with hydrogen in the presence of a catalyst urier high pressure. The resulting product is a glass-clear, pale yellow resin very resistant to oxidation.

In the isomerization process, liquid pine oil is treated with solid NaOH and the NaOH is subsequently removed by a series of washes.

Synthetic resins are manufactured by reacting refined rosins with various chemicals and compounds. The resins are made in heated kettles by reacting the rosins with glycerine, mono-, di- and triethylene glycol, ammonia, pentaerythritol, maleic anhydride, hydrogen, acetic acid, or other materials singly and in combination.

Metallic resinates are produced by reacting rosin with those metals which give soaps or salts that are water-insoluble. Limed rosin, zinc-treated rosin, and the resinates of lead, copper, cobalt and manganese, are of the greatest industrial importance.

Raw Materials and Products

Raw Materials

Raw materials needed for the primary processing of one ton of pine stumps are approximately as follows:

Pine stumps	One ton
Extraction solvent	100 - 600 gallons*
Water	2,000 - 5,000 gallons

* Re-used solvent; actual solvent loss ranges from 0.1 to 2.0 gallon per ton of chips.

Raw materials used in secondary refining are the rosins and oils from primary refining plus chemicals, compounds, and process water.

Products

Yields of finished products are difficult to report because of the wide variations in types of products manufactured and the processes employed. The yield also depends, to a great extent, on the rosin content of the wood processed, which varies with the locality from which the stumps were gathered. One ton of chips will usually yield 350 to 400 pounds of FF wood rosin and 85 pounds of terpene oils. The terpene oils average, by weight, 57 per cent turpentine, 36 per cent pine oil, and 7 per cent dipentene. On a volume basis, this is equivalent to 7 gallons of turpentine, 4 gallons of pine oil, and 1 gallon of dipentene per ton of chips processed.

In addition to refined rosins and oils, a few by-products are recovered and marketed. Dark, low-grade resins are sold for use in making foundry cores and in road building. Oil residues, known as "foots," can be used as disinfectants and cord preservatives.

Volume and Character of Wastes

Primary Process Wastes

Liquid wastes from the manufacture of steam-distilled wood naval stores will vary in volume and characteristics depending upon the processes employed and the deviations and modifications used at the different plants. Condition and efficiency of mechanical equipment will also influence the character and volume of process wastes.

Values considered to be representative of the volume and characteristics of these wastes are presented in Tables 1 and 2. Discussions of each of the wastes are presented in subsequent paragraphs.

(1) Stump Wash Water - This waste comprises the water used in washing the pine stumps prior to grinding and extraction. It contains large quantities of dirt, sand, and wood particles washed from the stumps. The characteristics of the waste depend upon the volume and force of the wash water used, and also upon the agitation the stumps receive during hauling and washing. B.O.D. values and suspended solids concentrations vary considerably. Caution must be taken in using B.O.D. values for this waste, as it contains wood fibers that are not easily broken down by microbiological action. In addition, this waste contains tannins, in solution, which are powerful reducing agents. All tannins are polyhydroxylic phenols and have bactericidal properties that not only affect the B.O.D. determinations but also the biology of the receiving stream. Stump wash water 5-day B.O.D. can be expected to vary between 50 and 1,500 parts per million. The volume of wash water at different plants ranges from 350 to 3,500 gallons per ton of stumps.

Table 1 - Representative Values of Character and Volume of Primary Process Naval Stores Manufacturing Wastes

Primary Process Waste Source	Discharge, gal/ton stumps		B.O.D., 5-day, 20°C.				Suspended Solids				*Population equivalent / Ton stumps	
			p. p. m.		lbs/ton stumps		p. p. m.		lbs/ton stumps			
	Naphtha Extraction	Benzene Extraction	Naphtha Extraction	Benzene Extraction	Naphtha Extraction	Benzene Extraction	Naphtha Extraction	Benzene Extraction	Naphtha Extraction	Benzene Extraction	Naphtha Extraction	Benzene Extraction
Stump Washer	(350-3,500)		(50-1,500)		(0.05-9.63)		(1,220-16,900)		(2.34-205)		(0.3-58)	
Drop Solution Wash	180		3,130		4.84		150		0.22		29	
Solvent Recovery	730	150	550	2,100	3.5	2.5	-	16	-	-	20	16
Oil Recovery	250	1,170	2,170	60	5.7	0.58	-	65	-	0.63	34	4
Furfuraldehyde Recovery		12		10,700		1.07		8		-		6

* Based on 0.167 pound 5-day B.O.D. per capita per day.

Table 2 - Representative Values of Character and Volume of Secondary Process Naval Stores Manufacturing Wastes

Secondary Process Waste Source	Unit	Discharge gal/unit	B.O.D., 5-day, 20°C.		Suspended Solids		*Population Equivalent / Unit
			p.p.m.	lbs/unit	p.p.m.	lbs/unit	
Pale Rosin Refining							
Solvent Recovery	1 ton	490	820	3.35	12	0.05	20.
Alcohol Recovery	stumps	485	385	1.55	24	.10	9.30
Polymerization							
Solvent Recovery	1000 lbs	2,100	75	1.33	28	.5	8
Acid Recovery	Rosin	750	17	.11	-	-	0.6
Disproportionation							
Condenser Water	1000 lbs	3,900	260	8.45	42	1.33	50
Alkaline Wash Water	Rosin	140	38,100	44.4	3,350	3.90	265
Hydrogenation	1000 lbs						
Waste Rosin Oils	Rosin	1	382,000	3.2	26,500	0.22	19
Synthesization	1000 lbs						
Condenser Water	Rosin	6,000	270	13.5	130	6.5	80
Isomerization	1000 gal.						
Wash Water	Pine Oil	500	14,800	49.3	75	0.25	295

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* Based on 0.167 pound 5-day B.O.D. per capita per day.

(2) Drop Solution Wash Water - This waste consists of wash water resulting from the washing of the crude rosin-oil-solvent solution prior to refining. It contains finely divided rosin (nigre), terpene oils, and solvent in suspension. The concentration of the waste depends upon the volume of water used in washing. Large volumes of water will give a dilute waste, but the total pollutional load will be increased. Suspended solids concentration of daily composites may vary as much as 100 per cent from the average. When benzene solvent is used as the extraction liquid, the drop solution is not washed before refining, but a small quantity of water separates from the solution in the drop tanks. The volume of this waste, however, is insignificant. Drop solution wash water, at one plant, accounted for 20 per cent of the total plant 5-day B.O.D.

(3) Solvent Recovery Waste Water - Liquid waste from the solvent recovery system consists of condenser water from low-pressure evaporators. It may contain some entrained solvent and oils. B.O.D. concentrations vary with the amount of water separated, and values of from 500 to 2,500 p.p.m. have been reported for this waste.

(4) Oil Recovery Waste Water - This waste consists of condenser water from fractional distillation units, and contains entrained terpene oils that are recovered when market conditions are favorable. B.O.D. values at one plant averaged 1,370 p.p.m. without oil recovery, and 490 p.p.m. with oil recovery. The volume of this waste may vary from 250 to 1,200 gallons per ton of stumps processed.

(5) Furfuraldehyde Recovery Waste Water - Furfuraldehyde is used in conjunction with the benzene extraction system as a selective

solvent to remove color bodies from refined rosin. This waste contains entrained oils that can be recovered. Furfural is also present but in concentrations of less than 10 p.p.m. B.O.D. values average 10,000 p.p.m. without oil recovery, and 3,000 p.p.m. with recovery.

Secondary Process Wastes

Secondary refining processes are presently carried out at only a few of the naval stores plants. All secondary refining units use as basic raw materials the rosins and oils obtained from primary processing. The wastes from these units are discussed in the following paragraphs.

(1) Polymerization Process - Two wastes are associated with this process: condenser water from sulfuric acid concentrators, and condenser water from solvent recovery evaporators. The acid concentrator waste has insignificant pollutional characteristics and is objectionable only because of the low pH, which remains about 3.0. Liquid wastes from the solvent recovery unit contains entrained solvent, acid and rosin oils. B.O.D. values range from 25 to 150 p.p.m. The pH will vary from 1.5 to 3.5.

(2) Disproportionation (Dehydrogenation) Process - The major wastes from this process are barometric condenser water from a vacuum system on the rosin distillation unit, and alkaline wash water from batch kettles. Both wastes contain finely divided rosin in suspension. B.O.D. values average 38,000 p.p.m. for the wash water and 260 p.p.m. for the condenser water. The volume of waste water discharged will vary with the type of soap or size produced.

(3) Hydrogenation Process - The liquid waste from this unit consists almost entirely of rosin oils. The volume of waste averages one gallon per 1,000 pounds of hydrogenated rosin produced. B.O.D. values average 382,000 ppm, suspended solids 26,500 ppm, and ether-extractable materials 467,000 ppm.

(4) Isomerization Process - Wastes from this unit comprise the water used in washing pine oil after treatment with hot caustic. B.O.D. values average 20,000 ppm for the first wash and 10,000 ppm for the second wash water. The volume of waste water averages 400 gallons for each wash.

(5) Synthesization Process - Waste water from synthetic resin manufacture includes quench water and condenser water. Wastes from this process will vary considerably in volume and characteristics, due to the numerous types of resins manufactured. B.O.D. values range from 130 to 700 ppm.

(6) Pale-Grade Rosin Refining Process - Liquid wastes from pale-grade rosin refining consist of condenser water from vertical tube evaporators. Two wastes are associated with this process: solvent recovery waste water, and alcohol recovery waste water. B.O.D. values from the solvent recovery units ranged from 50 to 5,000 ppm, and from the alcohol recovery units from 300 to 5,000 ppm.

(7) Metallic Resinate Manufacturing Process - Information concerning the wastes from this process were available from only one plant. Two wastes are present and originate from quench tanks and finishing stills. The combined waste flow amounts to only 12.5 GPM, but is objec-

tionable because of a high free acid content and high concentrations of toxic metallic ions.

(8) Miscellaneous Wastes - Other wastes of comparatively minor nature are those from washing tank cars, equipment and floors. Laboratory and pilot plant wastes also contribute to the total pollutional load. Tank car wash water normally contributes very little pollutional material, but on rare occasions may contribute as much as 10 per cent of the daily B.O.D. load of the plant.

Pollutional Effects

Liquid wastes from the manufacture of steam-distilled wood naval stores exert a deoxygenating effect on the receiving streams. In addition, the large quantities of suspended solids discharged cause sludge banks in the streams, which continuously reduce the dissolved oxygen. Wide variations in pH, together with the characteristic antiseptic qualities of these wastes, inhibit normal biological activity and may destroy aquatic life. Floating oil reduces reaeration and imparts a persistent turpentine taste and odor to the streams, which may be detrimental to their subsequent use.

Remedial Measures

Treatment of naval stores wastes has not been practiced by the industry, and very little is known concerning the effectiveness of physical, chemical, or biological treatment methods. Concerted effort is being made to solve the waste problems within the plant through changes in process. A few remedial measures have been proposed, including elimination, by-product recovery, equalization of flow, recirculation and re-use, and waste treatment where necessary.

Elimination

A logical procedure for reducing stream pollution is to eliminate offensive waste wherever possible. Certain low-volume, high-

concentration wastes can be disposed of by methods other than to receiving streams. In one instance, hydrogenation process waste, which was composed almost entirely of volatile oils, was disposed of by incineration rather than with the liquid wastes. Other wastes that can be eliminated from the plant sewers are small volumes of oil and resins remaining in returned tank cars. These volatile materials can be recovered for resale or disposed of by other methods.

By-Product Recovery

Recovery of by-products may be conducted for either of two reasons: (a) for the marketable products recovered, or (b) to eliminate pollution caused by their discharge into streams. At present, recovery is carried out by the industry only for the profit to be derived from their sale. An example can be cited where terpin hydrate, a by-product from crude oil refining, is recovered by one plant, only when the market is favorable. The B.O.D. of the waste carrying this product is reduced 60 to 65 per cent when the terpin hydrate is recovered. From the standpoint of stream improvement, it is desirable that this compound always be removed from the waste.

Equalization of Flow

This objective can best be carried out by lagooning where space is available. A two-fold benefit can be realized by lagooning naval stores wastes: (a) allowing settleable solids to accumulate, and (b) eliminating low-volume, high-concentration wastes from the

receiving streams. The tendency is to give an effluent with a relatively uniform concentration. Results of pH determinations on samples of the main effluent from one plant without storage showed variations in pH from 3.7 to 11.4.

A 90 per cent reduction in suspended solids was obtained in one instance by passing stump washer effluent through a settling basin having a detention period of less than 30 minutes.

Recirculation and Re-Use

Recirculation and re-use hold considerable promise as an economical means of alleviating some of the problems of naval stores wastes. Relatively clean condenser waters and wash waters may be re-used where they will not deleteriously affect process. Because most plants differ in process, the most effective re-use of waste waters is an individual plant problem. Aeration of process wastes before re-use has little or no effect on B.O.D. concentrations, but does exert a desirable cooling effect.

No data are available as to the total possible reduction in waste load that can be obtained by the various methods proposed and, even though the reduction must be considerable, there will remain some waste requiring additional treatment except where there is an abundance of dilution.

Waste Treatment

Treatment of wood naval stores wastes has been studied by Pyburn and Odom, Consulting Engineers, Baton Rouge, Louisiana. This research, recently conducted for and in co-operation with Newport Industries, Inc., Oakdale, La., plant, has shown that certain of these process wastes are amenable to biological oxidation on high capacity filters. Extended pilot filter operation has demonstrated consistent results and a treated waste acceptable for discharge to Calcasieu River.

The Oakdale plant produces rosin, pine oil, turpentine, dipentene, zinc resinates, and other terpene chemicals. Other specialty products may be manufactured at this plant when conditions warrant them. Wastes treated by the pilot plant originated from the primary process, with the stump wash waste excluded.

The first step in the waste treatment program was the segregation of process wastes, which required a major revision of the existing sewer system. Two metal gravity oil-water separators were installed in the sewer collection system near the waste sources. These separators were intended to provide prompt solvent recovery, thereby reducing the time of contact of the products with waste water. In addition, two concrete box pitch traps were provided to prevent clogging of sewers and the filter. These pitch traps were designed to permit withdrawal of heavy pitch from the bottom and lighter materials from the top, with separated water in continuous flow from the intermediate level. An

existing gravity-oil-water separator, located just upstream from the plant outfall, was used as a flow equalization tank and as an added safeguard against discharge of oils, solvents and terpene products originating from inadvertent spills. An 18-hour theoretical detention period, at the design flow of 90 GPM, is provided by the separator. Provision was also made to combine septic tank effluent with the wastes treated by the trickling filter as a means of providing continuous seeding.

The segregation of wastes resulted in four classifications, with separate treatment provided for the first three. These four waste classes were designated:

1. Stump wash
2. Nuroz unit
3. Primary process and storage tank
4. Miscellaneous

1. Stump Wash Waste - Stumps are washed on a two-shift, 16-hour per day basis. Liquid wastes from this process amount to about 250 GPM, or 480 gallons, per ton of stumps. The waste is currently being discharged to a sand pit where some filtration and sedimentation takes place. The effluent from this pit normally has a 5-day B.O.D. less than 35 ppm and averages 1,600 ppm suspended solids.

Plans for improved treatment of stump wash waste were prepared by engineering personnel of Newport Industries, Inc. It is proposed

to treat the waste by screening, coagulation, sedimentation, and re-use in a closed system. Coagulation, with lime, and sedimentation will take place in a clarifier equipped for mechanical collection and removal of sludge. It is planned to further dewater the sludge in settling ponds, with final disposal of sludge as fill in swampy areas near the plant. Make-up water will be added to replace that withdrawn with the sludge from the clarifier and to dilute out dissolved solids if necessary for satisfactory operation.

2. Nuroz Unit Waste - The Nuroz unit, which is a secondary process, produces a high-grade resin and resin products by a patented process using zinc chloride as a catalyst. Process wastes include a wash water containing free acid and a still waste high in zinc chloride. These wastes combined amounted to 12.5 GPM, with a zinc chloride concentration of 1.5 to 2.0 per cent.

Treatment of the Nuroz waste has been in effect for some time and consists of concentration by submerged combustion using an Ozark-Mahoning burner. This system of evaporation develops a thick jell which can be lagoned.

3. Primary Process and Storage Tank Wastes - These wastes originate from the extraction, separation and refining of crude terpene oils and rosin. These wastes were particularly significant in that 95 per cent of the total plant 5-day B.O.D. was contained in this flow of 105,000 gallons per day. It was this portion of the process waste that was treated on the biological filter pilot plant. Septic tank effluent

was added as a means of providing continuous seeding to the wastes applied to the filter. This partially treated sanitary sewage represented 4.3 per cent of the volume of the waste to be treated by the filter. The combined waste had an average 5-day B.O.D. of 4,500 ppm, negligible suspended solids, and a pH of 4.5.

4. Miscellaneous Wastes - This group of wastes was composed of those resulting from plant service. They included such wastes as boiler blowdown, water treatment plant sludge, and septic tank effluent. With the exception of septic tank effluent, the miscellaneous wastes were discharged without treatment.

Pilot Plant Studies

The pilot plant was placed in operation in December 1950. It has been operating since that time at various B.O.D. loadings, hydraulic loadings, and recirculation rates. The revised waste collection system, including pitch traps and oil-water separators, was completed prior to this date. Consequently a representative waste was supplied to the filter.

Pilot Plant Design

The pilot filter was 16 feet in diameter and 6 feet deep. Construction consisted of a wooden shell set on a 5-inch concrete slab. Blast furnace slag, 3/4 inch to 5 inches diameter, was used as filter media. Distribution of the waste on the filter was accom-

plished by means of a bronze spindle with a flared head "floating" in a vertical length of 1-1/2 inch pipe. Slanting grooves cut in the flared head of the spindle caused the spindle to rotate while discharging.

The humus tank was 3 feet in diameter with an operating water depth of approximately 3-1/2 feet. The recirculation pump took suction from this tank, thus returning some sloughed solids to the filter influent. In addition to providing acclimated seed for the filter, this system reduced the necessary capacity of the final clarifier.

Results

These studies indicated that an 83 per cent B.O.D. removal could be consistently obtained with a 5-day B.O.D. loading of 8,500 pounds per acre-foot per day. This was accomplished with an applied rate of 6.5 MGAD and a recirculation rate of 19 to 1. The maximum anticipated loading for design purposes was 10,000 pounds of 5-day B.O.D. per acre-foot per day.

The pilot filter was operated for a 10-day period at a B.O.D. loading of 28,000 pounds per acre-foot per day and a recirculation rate of 9 to 1. Under these conditions the over-all efficiency was 34 per cent. The highest B.O.D. loading during the period of investigation was 36,000 pounds 5-day B.O.D. per acre-foot per day. This was caused by a "slug" of caustic wash waste from tank cleaning. A 15 per cent reduction, without recirculation, was obtained from this shock load. During the studies the filter effluent averaged 765 ppm 5-day B.O.D.

for the loading rate of 8,500 pounds per acre-foot per day. This effluent mixed with the raw waste, having a concentration of 4,500 ppm 5-day B.O.D., and at the recirculation rate of 19 to 1, gave an applied waste with a 5-day B.O.D. of 950 ppm. The pH of the filter effluent was normally very close to 7.0. The rise in pH as the wastes passed through the filter was attributed to oxidation of organic acids.

Proposed Design

Based on this research, the final design contemplated one filter 150 feet in diameter and 6 feet deep. The design flow was 90 GPM of untreated waste and a 19 to 1 recirculation rate. The final clarifier allowed 1-1/2 hours' retention at the maximum anticipated flow of 115 GPM and provided an overflow rate of 600 gallons per square foot per day.

Summary

Naval stores are produced by the refining of oleoresinous materials from pine wood. The resulting products are rosin, turpentine and pine oil. Further refining of the basic products will yield additional commodities.

Volume and characteristics of the liquid wastes associated with the naval stores industry vary with production methods. The most voluminous and variable are those resulting from the steam and solvent extraction process.

The major liquid wastes resulting from the manufacturing of steam-distilled wood naval stores are as follows:

(1) Stump wash water used to clean the stumps prior to reduction and extraction.

(2) Drop solution wash water from washing the crude solution prior to refining.

(3) Solvent recovery waste water from low-pressure evaporators of the solvent recovery system.

(4) Oil recovery waste water from fractional distillation of crude terpene oils.

When benzene is used as the extraction solvent, the crude solution is further treated with furfuraldehyde to remove color bodies. This results in one additional waste flow:

(5) Furfuraldehyde recovery waste water from the solvent recovery system.

Liquid wastes from secondary manufacturing, produced on a limited scale in most plants, include the following:

(1) Polymerization process water from acid and solvent recovery units.

(2) Disproportionation (dehydrogenation) process water consisting of condenser and wash water.

(3) Hydrogenation process waste consisting of rosin oils from distillation units.

(4) Isomerization wash water from washing treated pine oil.

(5) Synthesization process water consisting of condenser and quench water.

(6) Alcohol recovery waste water from alcohol recovery stills of pale rosin refining units.

(7) Pale rosin refining waste water from pale rosin refining units.

(8) Metallic resinate process wastes consisting of wash water and quench water.

Considerable variations in volume and pollutional characteristics have been noted in certain waste components at different plants. The mechanical condition and skill in operation of refining units has a decided effect upon the characteristics of the resulting wastes.

Reduction or treatment of naval stores wastes has generally not been practiced by the industry. Recirculation after screening of stump wash water is practiced in some plants with a noticeable reduction in fresh water usage and waste water discharge. Pilot plant studies of waste treatment by trickling filter, conducted by one plant in Louisiana, indicate that an 83 per cent 5-day B.O.D. removal efficiency can be consistently obtained by this method. A few other remedial measures have been proposed, including: elimination,

by-product recovery, equalization of flow, and recirculation and re-use. Aeration of process wastes at two plants in Louisiana indicates little or no reduction in 5-day B.O.D.

Effort is being made to solve the waste problems within the plant before resorting to waste treatment processes and equipment.

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